

## Supporting Information

### Negating $\text{Na}||\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ Interfacial Resistance for Dendrite-Free and “Na-Less”

#### Solid-State Batteries

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#### Experimental Section

**Preparation of  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  Solid Electrolytes.** The  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  (NZSP) samples were synthesized via a conventional solid-state reaction method. The initial materials were  $\text{Na}_2\text{CO}_3$  (99.9%, Aladdin),  $\text{SiO}_2$  (99.9%, Aladdin),  $\text{ZrO}_2$  (99.99%, Aladdin),  $\text{NH}_4\text{H}_2\text{PO}_4$  (99.99%, Aladdin). 20% excess of  $\text{Na}_2\text{CO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  were used to compensate for the Na and P volatilization during the high-temperature calcination process. Stoichiometric amounts of the above chemicals were mixed and ground at 300 rpm for 24 h using a planetary ball mill (YXQM-1L, MITR, Changsha, China) with 5 and 10 mm  $\text{ZrO}_2$  balls and ethanol solvent in a  $\text{ZrO}_2$  jar. Subsequently, the ball-milled mixture was dried in a vacuum oven at 80 °C for 4 h before it was preheated at 600 °C for 4 h and calcined at 1150 °C for 4 h in air. The calcined powder was ground in an agate mortar, and then ball-milled again for 2 h at 450 rpm. The obtained powder was dried and pressed uniaxially (5 metric tons, YLJ-15T-LD, MTI Corp., Hefei, China) to form green pellets of 10 mm diameter and 1 mm thickness, which were further densified using a cold isostatic press (YLJ-CIP-15, MTI Corp., Hefei, China) under 200 MPa. Finally, the pellets were sintered at 1200 °C for 6 h in an alumina crucible in air. In order to prevent Na and P loss during sintering, all NZSP pellets were placed over a powder bed of identical composition in the bottom of the crucible to prevent reactions with alumina and covered by the same powder to reduce Na/P loss during sintering. All heating and cooling rates were set at 5 °C/min. To avoid reactions with moisture or carbon oxides in the air, the sintered NZSP pellets were transferred to and stored in an Ar-filled glovebox for further use.

***Pb/C surface modification.*** 10  $\mu\text{L}$  aqueous solution of saturated  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$  was drop on the surface of a NZSP pellet and distributed evenly using a brush. For samples used in symmetrical cell testing, both sides of NZSP pellets were coated with  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$  using the same method. After drying, the coated NZSP pellets were transferred into a tube furnace and heated at 550  $^\circ\text{C}$  for 5 h under Ar flow. The carbon-coated NZSP was prepared by following the same protocol but with a  $\text{NaAc} \cdot 3\text{H}_2\text{O}$  precursor. To reduce exposure to air, the quartz tube containing the treated pellets was transferred into a glove box immediately after the samples were cooled to 90  $^\circ\text{C}$ .

***Preparation of NVP/C cathode.*** In a typical synthesis, 15 mmol  $\text{Na}_2\text{CO}_3$  (99.9%, Aladdin), 10 mmol  $\text{V}_2\text{O}_5$  (99%, Energy Chemical), 30 mmol  $\text{NH}_4\text{H}_2\text{PO}_4$  (99.99%, Aladdin), and 1 g  $\text{C}_6\text{H}_{12}\text{O}_6$  (99%, Sinopharm Chemical Reagent Co., Ltd.) were ball-milled for 12 hours at 300 rpm in ethanol using an alumina jar. The obtained mixture was uniaxially pressed into a pellet that was subsequently annealed at 450  $^\circ\text{C}$  for 4 h under Ar flow. After cooling, the precursor pellet was crushed and ball-milled again in ethanol at 300 rpm for 12 hours using an alumina jar. Finally, the NVP/C sample was produced by calcinating the dry precursor powders at 800  $^\circ\text{C}$  for 24 h in Ar. To fabricate NVP/C electrodes, a slurry of the NVP/C powder, Super P (MTI Corp., Shenzhen), and PVDF (Kynar HSV 900) at a weight ratio of 70: 20: 10 was cast onto carbon-coated Al foil (MTI Corp., Shenzhen, 18 mm in thickness). The electrode material loading is about 2-3  $\text{mg cm}^{-2}$ .

***Preparation of S cathode.*** The  $\text{Fe}_3\text{C}$ - and nitrogen-doped carbon at activated porous carbon cloth ( $\text{Fe}_3\text{C}\text{-NC@ACC}$ ) matrix was prepared using a previously reported method.<sup>[1]</sup> The activated porous carbon cloth was prepared by a simple alkaline activation treatment on commercial carbon cloth. Typically, a piece of ACC was immersed in 40 mL DI water that contains 0.5 mL pyrrole monomer and 0.8 mL hydrochloric acid solution. 1.0 g of potassium ferricyanide was added into 10 mL DI water under stirring. After cooling down to about 4  $^\circ\text{C}$ ,

both solutions were mixed together and kept at 4 °C for 4 h. The resultant carbon cloth was washed by DI water and dried at 60 °C, followed by annealing at 800 °C for 2 h in N<sub>2</sub>. Subsequently, sulfur was loaded on the carbon composite scaffold according to a simple inside encapsulation method to obtain S/Fe<sub>3</sub>C-NC@ACC. The carbon matrix was immersed in the sulfur/CS<sub>2</sub> solution until the mixture was completely dry. Then, the mixture was transferred into a sealed glass bottle filled with argon and heated at 155 °C for 10 h. The sulfur contents in the composite sample were about 1.0 mg/cm<sup>2</sup>. Finally, the sulfur cathode in solid state was prepared by mixing 80 wt% S/Fe<sub>3</sub>C-NC@ACC and 20 wt.% PEO10-NaFSI in acetonitrile. The PEO10-NaFSI was prepared by mixing 40 wt.% NaFSI and 60 wt.% PEO (M.W.: 5,000,000, Sigma-Aldrich) in acetonitrile and stirred at 60 °C for at least 24 h in Ar-filled glove box.

**Physicochemical characterizations.** XRD patterns were collected using an X-ray diffractometer (SmartLab9 KW) at a scan rate of 10° min<sup>-1</sup> in the 2θ range of 10-80°. The microstructural and composition analysis of the powders and fractured cross-sections of NZSP pellets were conducted on a field emission scanning electron microscope (SEM, Hitachi S4800) equipped with an energy dispersive spectrometer (EDS). Surface chemical states of NZSP pellets were identified by X-ray photoelectron spectroscopy (XPS, PHI QuanteraII) on an X-ray photoelectron spectrometer with Al Kα as the X-ray source, and all binding energies of samples were corrected by referencing the C 1s peak to 284.8 eV. An *in-situ* heating kit (Beijing Scistar Technology) was used for the *in-situ* Raman study on the decomposition process of Pb(Ac)<sub>2</sub>·3H<sub>2</sub>O coated on NZSP pellets. Raman spectra were collected on a Via-Reflex Raman spectrometer (HORIBA XploRA PLUS, Japan) equipped with a 50 × -LWD objective and laser at 638 nm with 8 mW laser power. The time acquisition was 10 s and 10 scans were recorded to improve the signal-to-noise ratio. For contact-angle measurements, NZSP pellets were preheated on a hot plate at 120 °C inside the glovebox, and a small piece of Na metal (oxidation layer pre-removed) was placed on top of NZSP pellets to allow the observation of wetting

phenomena.

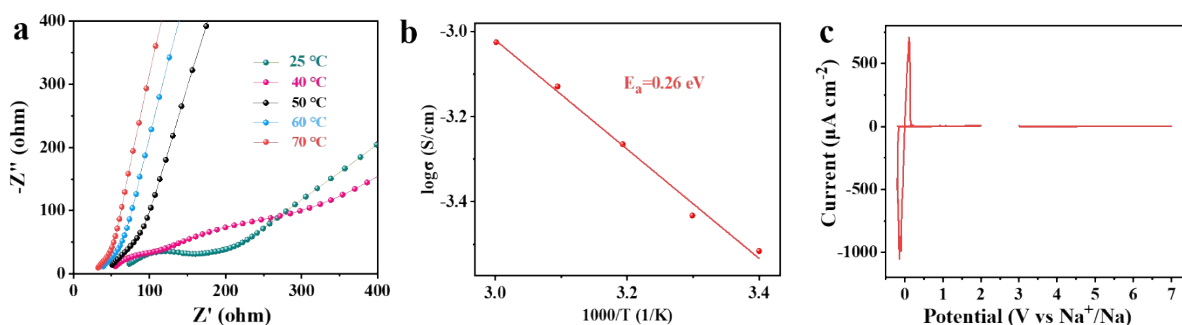
**Electrochemical Testing.** The ionic conductivity of NZSP pellets was determined by AC impedance measurements conducted on a Gamry REF 600+ potentiostat/galvanostat (Gamry, USA) using an Au||NZSP||Au configuration from 5 MHz to 1 Hz with an amplitude of 10 mV. For the assembly of Na||NZSP||Na symmetric cells, two Na disks (diameter: 9 mm) were hand-pressed on both sides of the NZSP pellet. For the assembly of Na||Pb/C@NZSP||Na cells, Na was preloaded on both sides of the Pb/C@NZSP pellet by a molten Na infusion process. All Na symmetric cells were assembled using a pressure-controllable Swagelok-type cell holder (EQ-PSC, MTI Corp.). The stacking pressure control was enabled with the help of a uniaxial press equipped with a pressure sensor (YLJ-5T, MTI Corp.). To be specific, the pressure sensor reads the mass load ( $m$ ) in kg, which can be converted to the pressure applied on the NZSP pellet based on  $P=mg/A$ , where  $A$  is the effective area of the pellet. For instance, a stacking pressure of 15 MPa used in the present work was estimated based on the reading load (120 kg) and the pellet area (0.8 cm<sup>2</sup>):

$$P = (120 \text{ kg} * 10 \text{ m/s}^2) / 0.8 \text{ cm}^2 = 1500 \text{ N/cm}^2 = 15 \text{ MPa}.$$

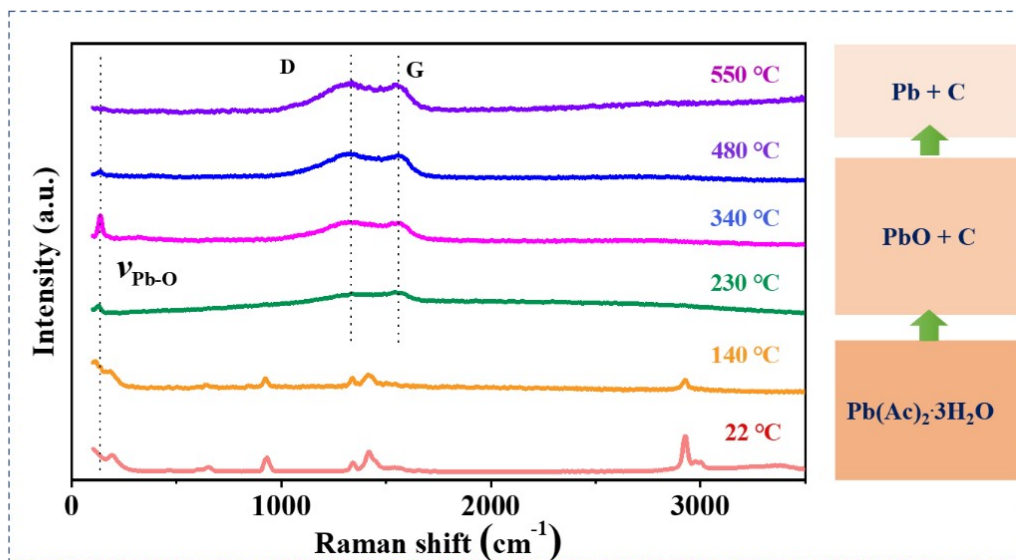
The impedance measurements were carried out over a frequency range of 5 MHz to 1 Hz with a 10 mV amplitude. All EIS spectra were analyzed and fitted by a Z-view software. For NVP-based full cells, 10  $\mu$ L liquid electrolyte (1 M NaClO<sub>4</sub> in EC/DMC (1:1) + 5% FEC) was used to improve the cathode interface contact. For S-based solid-state cells, S cathodes were assembled directly with the NZSP solid electrolyte without liquid electrolyte. For NZSP based full cells, a Na disk was hand press on the anode side; for Pb/C@NZSP based full cells, Na anode was fabricated by pre-infusing molten Na into the Pb/C modified side. All full cells were assembled in an argon-filled glove box ([H<sub>2</sub>O] < 0.1 ppm, [O<sub>2</sub>] < 0.2 ppm) at room temperature using a coin-cell configuration and cycled using a NEWARE-BTS battery tester (NEWARE, Shenzhen). An incubator (Neware CT-9004, 25 °C) was used for temperature control unless

mentioned otherwise.

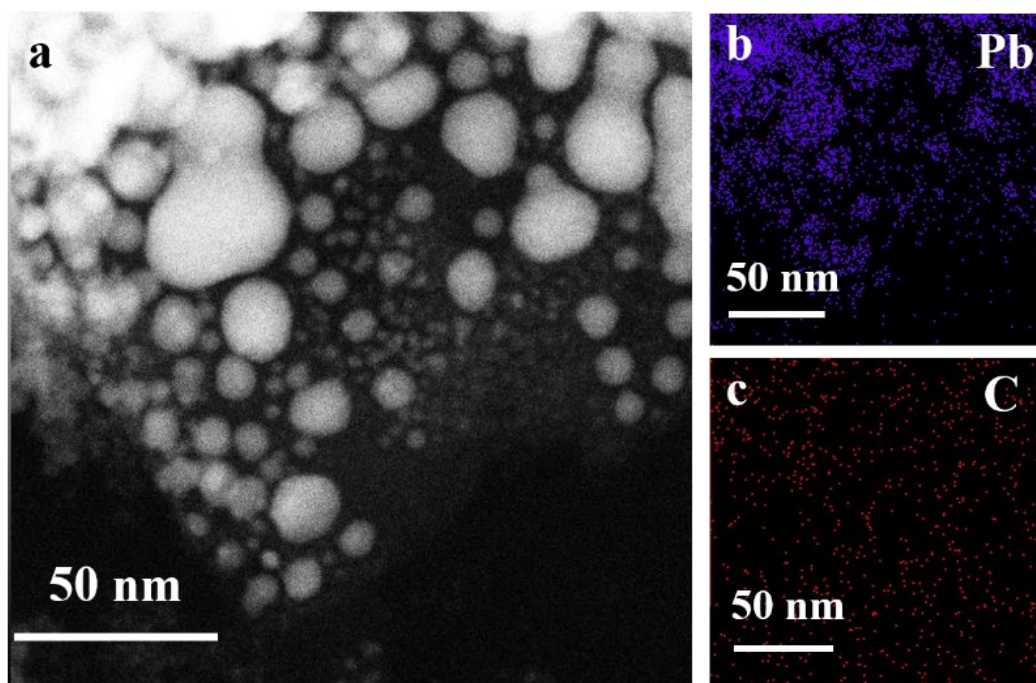
**Density Functional Theory (DFT) Calculations.** All DFT calculations were performed with the VASP code,<sup>[2]</sup> Projector Augmented Wave (PAW) methods were used for the pseudopotentials.<sup>[3]</sup> The generalized gradient approximation (GGA) with the Perdew-Burke-Emzerhof (PBE) functional was employed to describe the exchange correlation energy.<sup>[4]</sup> The energy cutoff was set to 450 eV. The convergence criterion for the electronic self-consistency loop and atomic forces was set to  $10^{-5}$  eV and  $0.05$  eV  $\text{\AA}^{-1}$ , respectively. To simulate the interface of Na/Pb, Na/NZSP, Na/ $\text{Na}_2\text{CO}_3$  and Na/C, the lattice constant of four layers of Na (001) slab was adjusted to adapt the dimensions of Pb (001), NZSP (001),  $\text{Na}_2\text{CO}_3$  (001) and C (001). The number of atoms in these interfaces and the lattice parameters for the interfaces are listed in **Table S3**. A vacuum region of  $15$   $\text{\AA}$  was set along the z direction and the back half atoms that are farthest away from the interface in each slab were fixed for all the heterostructure geometry optimizations. A  $1 \times 1 \times 1$  k-point mesh was used for the Brillouin Zone sampling to speed the optimization process.



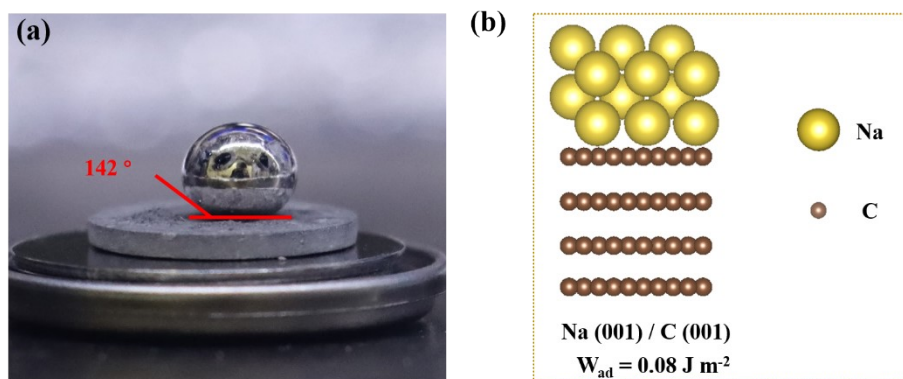
**Figure S1.** (a) Evolution of impedance spectra with temperature, and (b) the corresponding Arrhenius plot of the NZSP pellet. (c) CV curves of a Na||NZSP||Au cell within -0.2-2.0 V ( $0.3$   $\text{mV s}^{-1}$ ) and 3.0-7.0 V ( $0.05$   $\text{mV s}^{-1}$ ).



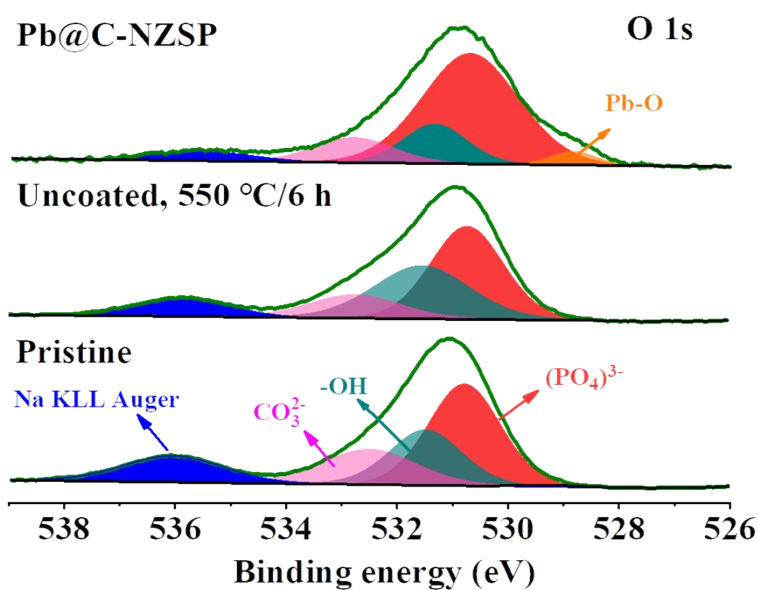
**Figure S2.** In-situ Raman spectra for the annealing process of  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$  conducted from 22 °C to 550 °C.



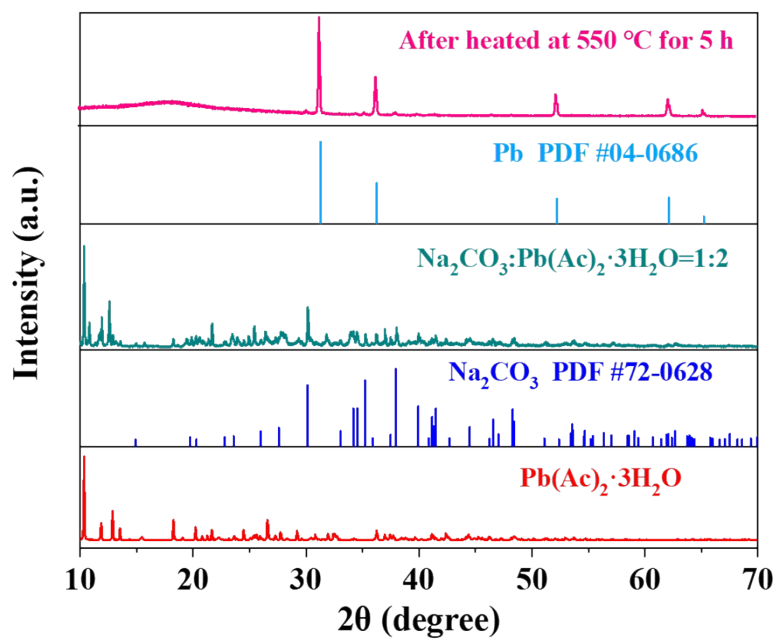
**Figure S3.** TEM and EDX images of the Pb/C sample scratched from the Pb/C@NZSP surface.



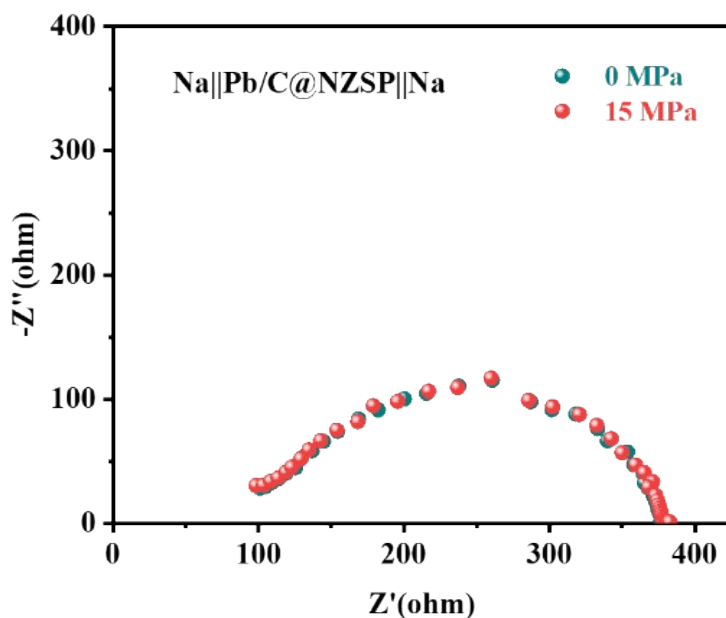
**Figure S4.** (a) Contact-angle measurement of molten Na on the carbon-coated NZSP surface. (b) Theoretical structure simulation and work of adhesion ( $W_{ad}$ ) values for the Na(001)/ C(001) interface.



**Figure S5.** High-resolution XPS spectra of O 1s acquired on the surfaces of the pristine NZSP, NZSP heated at 550 °C for 5 h in Ar, and Pb/C@NZSP.

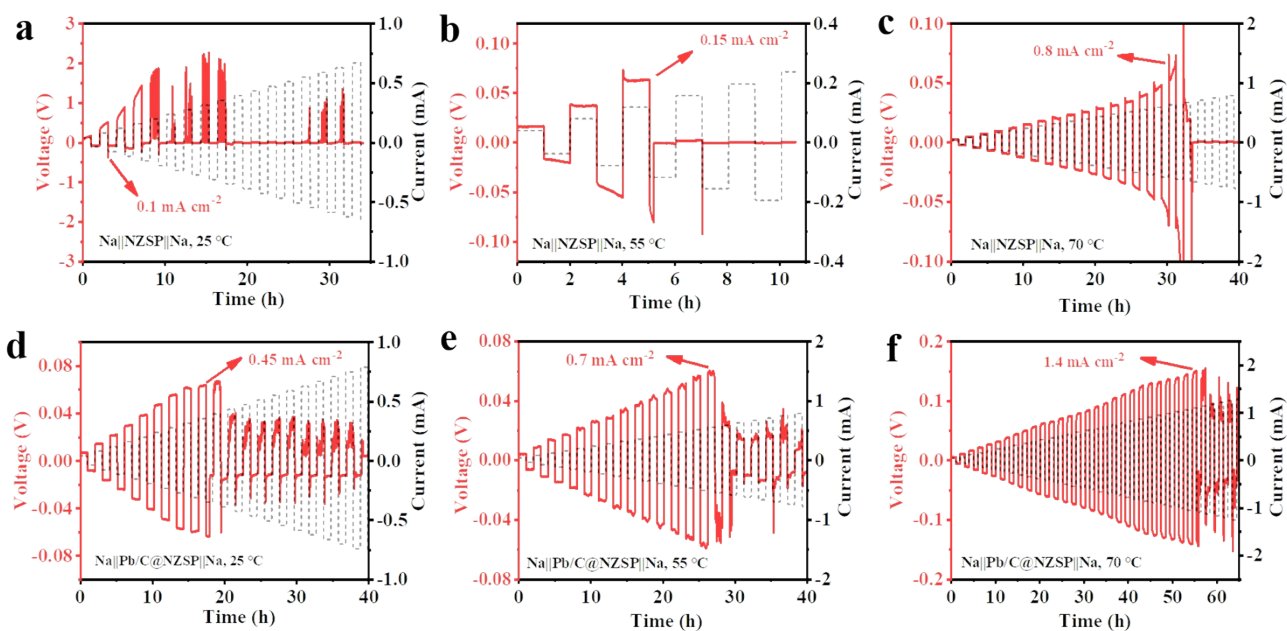


**Figure S6.** XRD diffraction patterns of the powder mixture (the weight ratio of  $\text{Na}_2\text{CO}_3$  to  $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$  is 1:2) before and after annealing at 550 °C for 5 h under Ar flow.

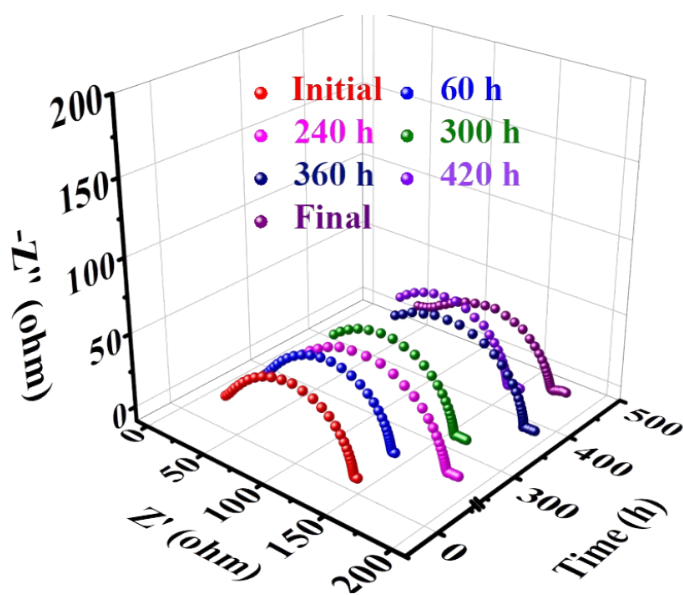


**Figure S7.** EIS spectra of  $\text{Na}||\text{Pb}/\text{C}@\text{NZSP}||\text{Na}$  symmetrical cells measured at 25 °C with different stacking pressures of 0 MPa and 15 MPa.

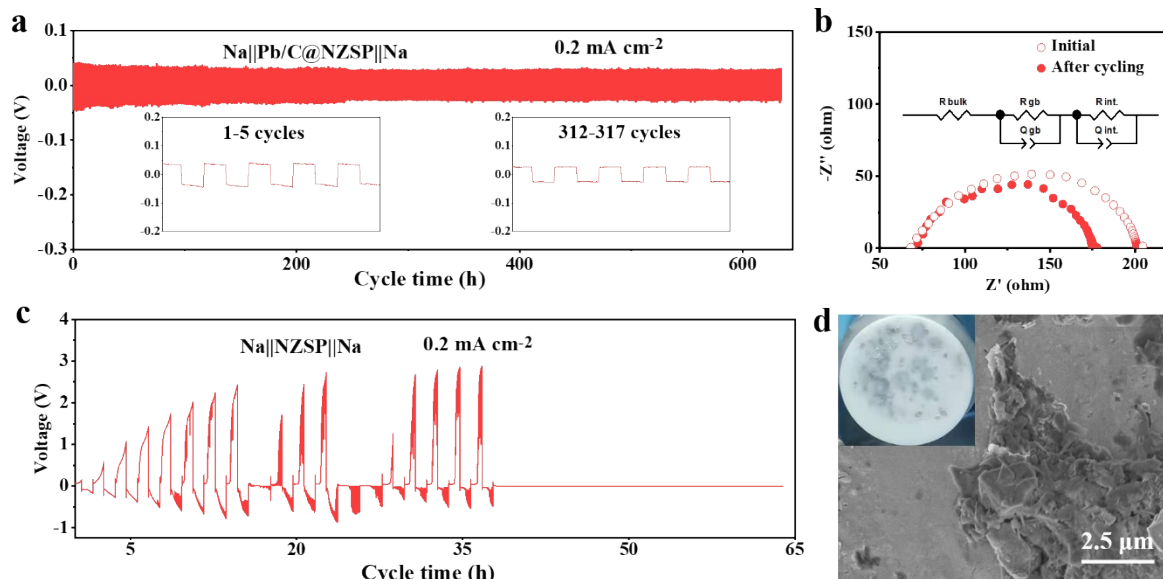




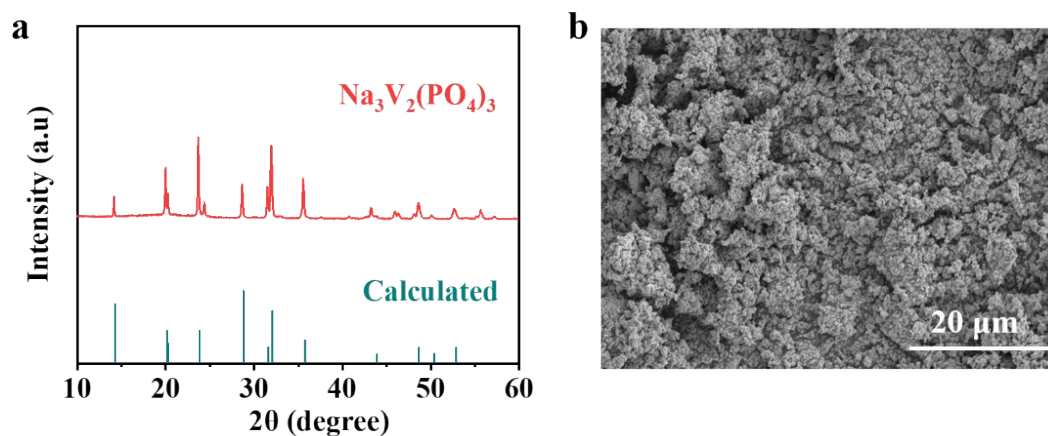
**Figure S8.** The CCD measurement profiles of (a-c) Na||NZSP||Na and (d-f) Na||Pb/C@NZSP||Na symmetric cell at 25 °C, 55 °C, and 70 °C.



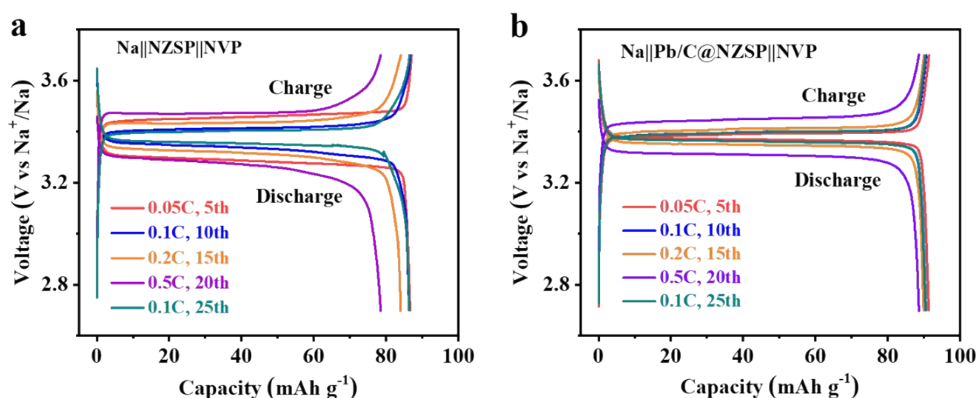
**Figure S9.** EIS spectra for the Na||Pb/C@NZSP||Na cell from 0.05-0.7 mA cm<sup>-2</sup> at 55 °C.



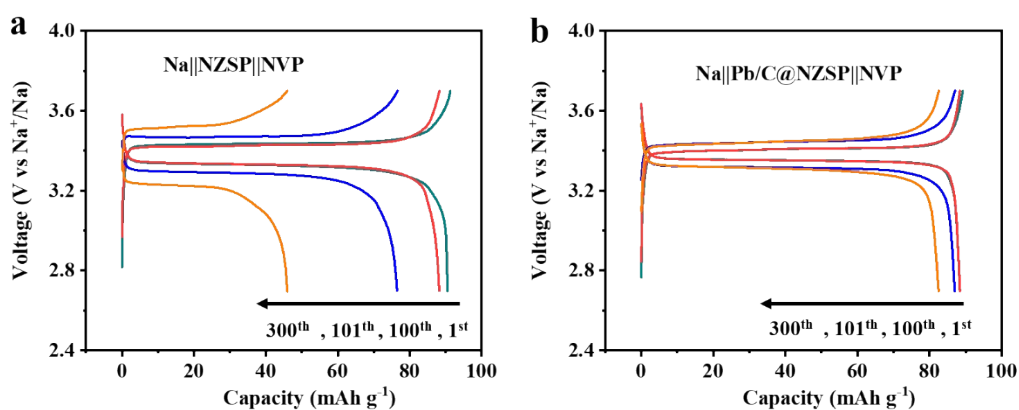
**Figure S10.** (a) Galvanostatic cycling curves of the Na||Pb/C@NZSP||Na symmetrical cell at  $0.2 \text{ mA cm}^{-2}$  at  $25 \text{ }^\circ\text{C}$ . (b) EIS spectra of the Na||Pb/C@NZSP||Na symmetrical cell before and after cycling at  $0.2 \text{ mA cm}^{-2}$ . (c) Galvanostatic cycling curves of the Na||NZSP||Na symmetrical cell at  $0.2 \text{ mA cm}^{-2}$  at  $25 \text{ }^\circ\text{C}$ . (d) SEM image and digital photo taken on the NZSP pellet surface after the cell failure originating from dendrite growth.



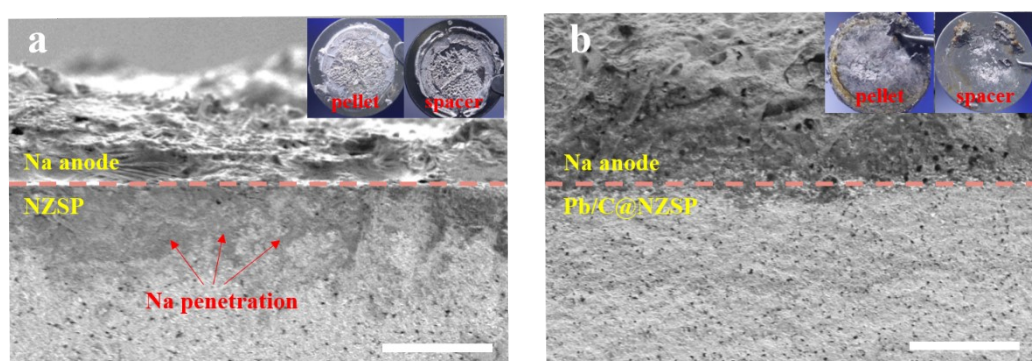
**Figure S11.** (a) XRD pattern and (b) SEM image of as-synthesized  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  powders.



**Figure S12.** The charge/discharge curves of (a) Na||NZSP||NVP and (b) Na||Pb/C@NZSP||NVP cells for the last cycle of 0.05C, 0.1C, 0.2C, 0.5C and 0.1C during rate capability tests.

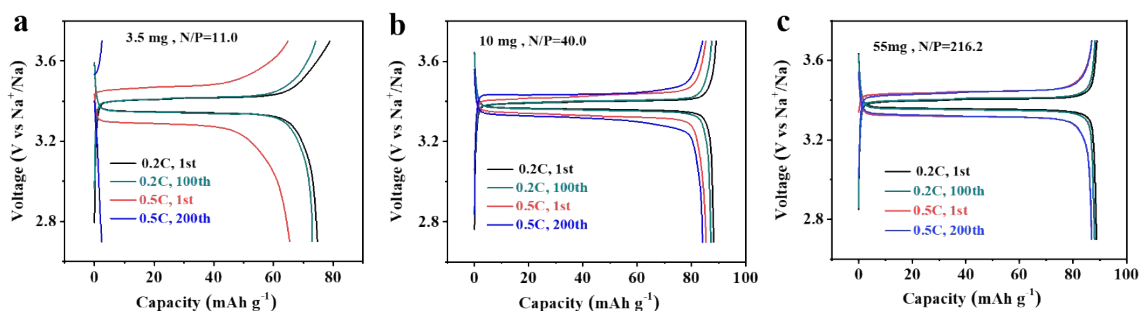


**Figure S13.** The charge/discharge curves of (a) Na||NZSP||NVP and (b) Na||Pb/C@NZSP||NVP cells for the initial and last cycle at 0.2C (100 cycles) and 0.5C (200 cycles).

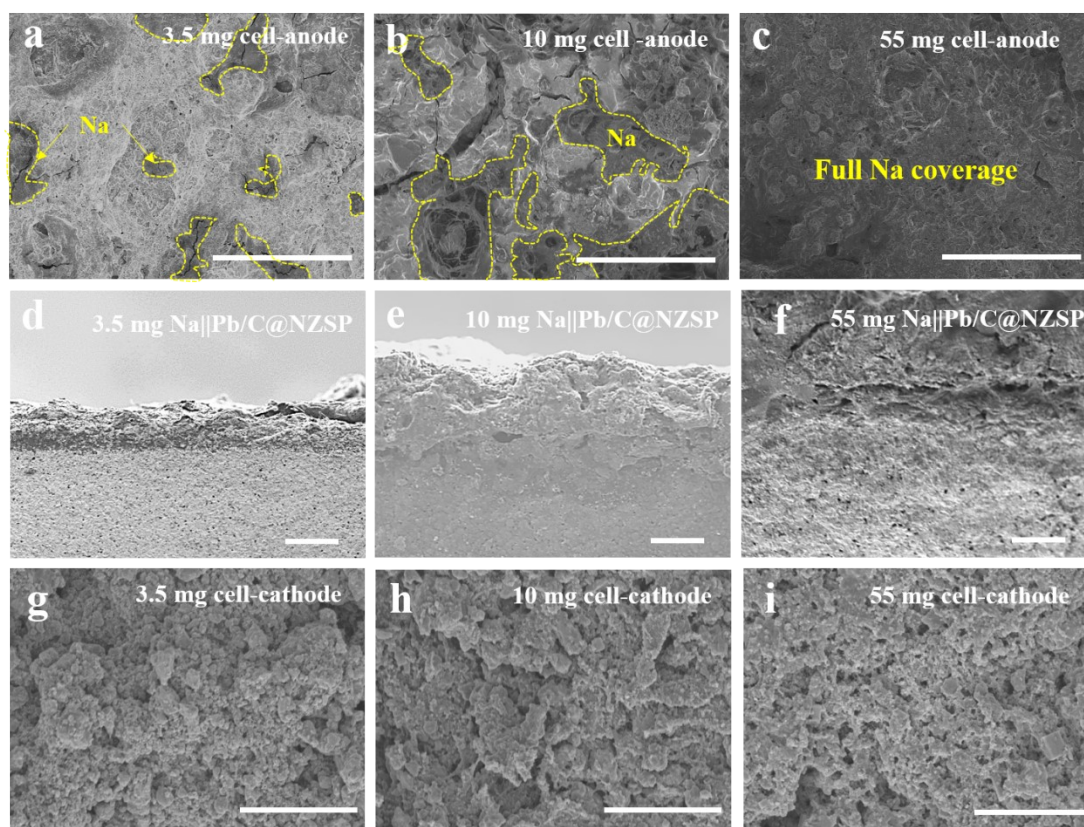


**Figure S14.** Postmortem SEM characterizations conducted on the anode interfaces of the cycled (a) Na||NZSP||NVP and (b) Na||Pb/C@NZSP||NVP cells. Insets show the corresponding digital

images taken on both pellet and spacer sides. Scale bars: 100  $\mu\text{m}$ .

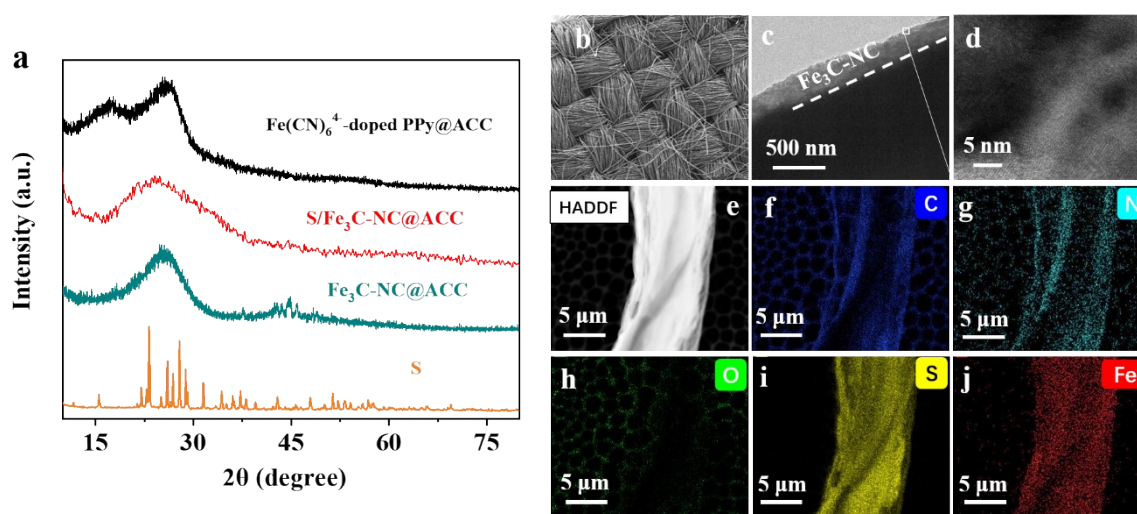


**Figure S15.** The charge/discharge curves of Na||Pb/C@NZSP||NVP cells with different Na loadings, or various N/P ratios: (a) N/P=11.0, (b) N/P=40.0, and (c) N/P=216.2.

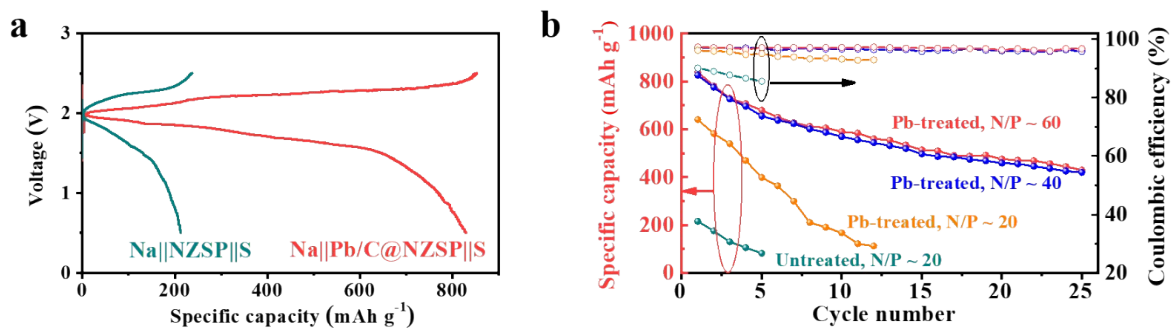


**Figure S16.** Postmortem SEM characterizations conducted on the (a-c) Na anode surfaces, (d-f) Na||Pb/C@NZSP cross-sections and (g-i) NVP cathode surfaces of the cycled Na||Pb/C@NZSP||NVP cells loaded with (a, d, g) 3.5, (b, e, h) 10, and (c, f, i) 55 mg Na. Scale

bars: 100  $\mu\text{m}$  for **a-f** and 5  $\mu\text{m}$  for **g-i**.



**Figure S17.** (a) XRD diffraction patterns of S, Fe<sub>3</sub>C-NC@ACC, S/Fe<sub>3</sub>C-NC@ACC and Fe(CN)<sup>4-</sup>-doped PPy@ACC. (b) SEM, (c-d) HAADF-STEM images and (e-j) the corresponding EDX mappings of S/Fe<sub>3</sub>C-NC@ACC.



**Figure S18.** (a) The 1st charge/discharge curves of Na||NZSP||S and Na||Pb/C@NZSP||S batteries. (b) The cycling performances of Na||Pb/C@NZSP||S batteries under different N/P ratios of 20, 40, and 60.

**Table S1.** The fitting results of EIS spectra acquired on different Na symmetric cells.

Symmetric cell	$R_b$ (ohm)	$R_{gb}$ (ohm)	$C_{gb}$ (F)	$R_{int}$ (ohm cm <sup>2</sup> )	$C_{int}$ (F)
NZSP, 0 MPa	51.86	120.6	$5.53 \times 10^{-9}$	391	$5.15 \times 10^{-8}$
NZSP, 15 MPa	85.69	80.94	$9.53 \times 10^{-10}$	87.5	$3.07 \times 10^{-8}$
Pb/C@NZSP	81.57	88.86	$9.19 \times 10^{-10}$	1.5*	/

**\*Note:** The effective area used for calculating  $ASR_{int}$  is 0.8 cm<sup>2</sup>. For the Na||Pb/C@NZSP||Na cell, the grain boundary and interface contribution cannot be separated as shown in Fig. 3b. Therefore, the  $R_{int}$  of 3.72  $\Omega$  was estimated by subtracting the total cell resistance ( $R_b + R_{gb}$ ) of 170.43  $\Omega$  by the total resistance of the NZSP pellet (166.71  $\Omega$ , Fig. S1).

**Table S2.** Fitted cell resistances from EIS analysis of full cells shown in Fig. 5d-f.

Cell notation	$R_{Cell}$ , initial ( $\Omega$ )	$R_{Cell}$ , after 0.2C ( $\Omega$ )	$R_{Cell}$ , after 0.5C ( $\Omega$ )
3.5 mg	321.7	413.7	675.3
10 mg	207.7	228.6	308.0
55 mg	262.4	349.1	434.5

**Table S3.** Summary of parameters of different interfaces for DFT calculations.

Interfaces	No. of Atoms	a/ $\text{\AA}$	b/ $\text{\AA}$	$W_{ad}/J m^{-2}$
Na (001)/ NZSP (001)	192	9.1187	18.2388	0.25
Na (001)/ Pb (001)	292	20.2485	20.2485	0.44
Na (001)/ Na <sub>2</sub> CO <sub>3</sub> (001)	160	18.1879	5.3007	0.12
Na (001)/ C (001)	92	4.2608	12.3000	0.08

## References

- [1] K. Lu, H. Zhang, S. Gao, H. Ma, J. Chen, Y. Cheng, *Advanced Functional Materials* **2019**, 29, 1807309.
- [2] Kresse, Furthmuller, *Physical review. B, Condensed matter* **1996**, 54, 11169.
- [3] Perdew, Burke, Ernzerhof, *Physical review letters* **1996**, 77, 3865.
- [4] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys Rev B Condens Matter* **1992**, 46, 6671.